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Antarctic ozone depletion and its correlation with solar flare numbers

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Abstract : A critical study of Antarctic ozone depletion and its correlation with solar flare numbers are performed. It is shown that yearly variation of O_3-concentration in D.U. and solar flare numbers are mainly controlled by their October concentrations and the nature of variation of O_3-concentration with solar flare number is oscillatory. It has slightly increasing tendency with the increase of solar flare number. One possible explanation of dramatic decrease of O_3-concentration at Antarctica during Antarctic Spring is also presented.

Keywords : Ozone depletion, solar flare number.

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1. Introduction

Recent ozone assessment confirmed that O_3 is slowly declining everywhere but dramatic decrease of O_3-concentrations takes place at Antarctica during spring time. It was first reported by Farman *et al* [1] in the year 1985. Afterwards, it was verified by different investigators throughout the world. In our previous publication [2], we have presented different theories proposed by different investigators throughout the world for the dramatic decrease of O_3-concentration at Antarctica. Chemical, natural and dynamical theories are mainly important.

i) *Chemical theory* – According to this theory, different chemical reactions are responsible for dramatic decrease of O_3-concentration at Antarctica during spring time. The chemicals which catalyse these reactions are O_x, HO_x, ClO_x, BrO_x, CHO_x, SO_x *etc.* and PSCs [2,3,4].

The reaction is endothermic. So higher temperature will favour the higher equilibrium concentration of ozone. If the temperature decreases, the rate of formation of O_3 also will decrease. During the month of October, the temperature achieves its lowest value [10], so the

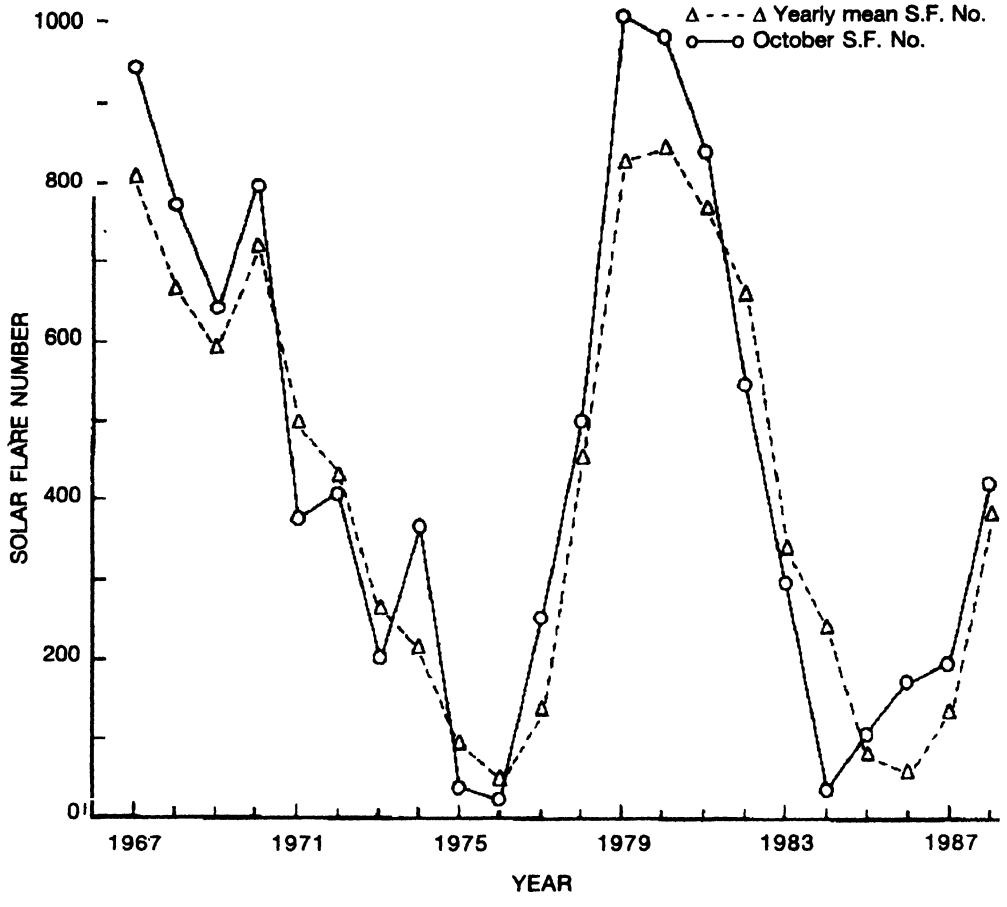

Figure 2. Yearly mean S.F. No. and October S.F. No. variation for different years.

formation of O_3 will also achieve its minimum value. Again at the low temperature, the reaction rate both for formation and depletion of ozone will decrease. But due to the presence of pollutants *e.g.* freon, the atomic chlorine, odd nitrogen oxides, OH radicals *etc.* the ozone is depleted by the same rate. Hence, the rate of depletion becomes predominant. Ozone depletion mechanisms are as follows :

Chlorine catalysed ozone depletion given by Molina and Rowland [11] is

$$Cl + O_3 \longrightarrow ClO + O_2$$

$$ClO + O \longrightarrow Cl + O_2$$

$$\text{Net}: O_3 + O \longrightarrow O_2 + O_2.$$

Molina and Molina [12] suggested that a ClO dimer was also involved :

$$ClO + ClO + M \longrightarrow (ClO)_2 + M$$

$$(ClO)_2 + h\nu \longrightarrow Cl + ClOO$$

$$ClOO + M \longrightarrow Cl + O_2 + M$$

$$2 \times (Cl + O_3 \longrightarrow ClO + O_2)$$

$$\text{Net}: 2O_3 \longrightarrow 3O_2,$$

where $h\nu$ represents of UV photon and M signifies a collisional chaperone either N_2 or O_2.

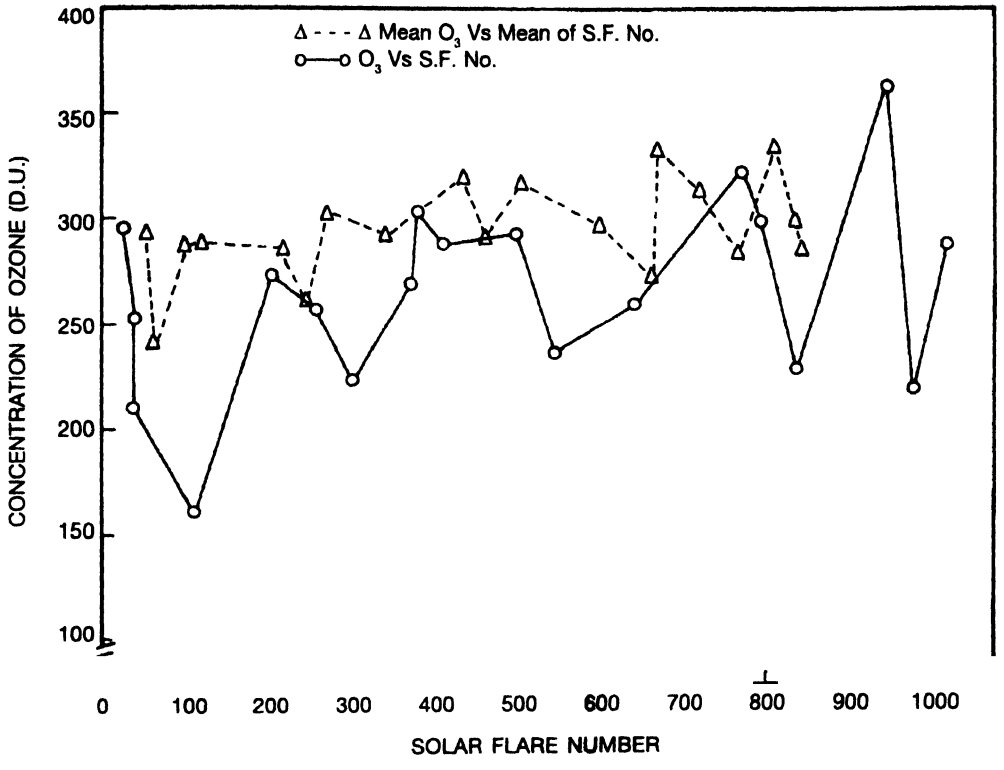

Figure 3. Plot of yearly mean ozone concentration in D.U. against yearly mean S.F. No (Δ - - - - Δ) and plot of October O_3 concentration in D.U against October S.F. No. (O - - - - - - O).

McElroy [13] suggested chlorine and bromine both catalysed O_3 destruction as follows :

$$ClO + BrO \longrightarrow Cl + Br + O_2$$

$$Cl + O_3 \longrightarrow ClO + O_2$$

$$Br + O_3 \longrightarrow BrO + O_2$$

$$\text{Net}: 2O_3 \longrightarrow 3O_2.$$

Solomon *et al* [14] suggested Cl and OH radical catalysed ozone depletion as follows :

$$HO_2 + ClO \longrightarrow HOCl + O_2$$

$$HOCl + h\nu \longrightarrow OH + Cl$$

$$Cl + O_3 \longrightarrow ClO + O_2$$

$$OH + O_3 \longrightarrow HO_2 + O_2$$

$$\text{Net}: 2O_3 \longrightarrow 3O_2.$$

From above mechanism, it is clear that atomic oxygen is not involved in O_3 destruction. It is supported by the fact that the atomic oxygen concentration is very low in the polar stratosphere. The concentration is reduced because of lack of UV-radiation in late winter.

The polar stratospheric clouds (PSCs) now play the key role for the spring time destruction of ozone and the formation of the ozone hole [15]. Under normal winter conditions in the lower stratosphere, the temperature fall low enough within the polar vortex such that the clouds of nitric acid trihydrate (NAT) and ice can form despite the dryness of the stratosphere. These clouds are generally referred to as polar stratospheric clouds [16]. They are the sites for a group of heterogeneous reactions that perturb the normal gas-phase chemistry in the polar region. The sequence of reactions are as follows :

At temperature dropping to or below 195K, NAT and ice particles are formed. HCl then dissolves along the grain boundaries in ice particles. The unreactive chlorine species, chlorine nitrate ($ClONO_2$) and hydrochloric acid (HCl), the dominant chlorine reservoirs react at the particle surface forming molecular chlorine gas and nitric acid.

$ClONO_{2(g)} + HCl_{(s)} \xrightarrow{M} Cl_{2(g)} + HNO_{3(s)}$, where M is a third body molecule or particle. The other two reactions [17] are :

$$ClONO_2 + H_2O \longrightarrow HCl + HNO_3,$$

$$HOCl + HCl \longrightarrow Cl_2 + H_2O.$$

The molecular chlorine is photolysed in the spring sunlight and atomic chlorine is released in the gas-phase. $Cl_2 + h\nu \rightarrow Cl + Cl$. It on reaction with ozone, initiates the catalytic chains.

Due to reactions

$$O_3 + h\nu (\lambda < 320\ \text{nm}) \longrightarrow O(^1D) + O_2,$$

$$O(^1D) + H_2O \longrightarrow 2OH,$$

where h is Plank's constant, ν is the frequency, and λ is wavelength, ozone becomes the precursor for OH radicals, the main oxidizing agent in the atmosphere [18]. In the stratosphere, photolysis of molecular oxygen forms O_3 of which a fraction is transported mostly to the

extratropical troposphere [19]. In the troposphere, in addition, the following reactions are responsible for O_3 destructions [20] :

$$CO + OH \longrightarrow H + CO_2$$

$$H + O_2 + M \longrightarrow HO_2 + M$$

$$HO_2 + O_3 \longrightarrow OH + 2O_2$$

$$\text{Net}: O_3 + CO \longrightarrow CO_2 + O_2 .$$

In presence of "sufficient concentration of NO", the formation of ozone is favoured as given by Crutzen [21].

$$CO + OH \longrightarrow H + CO_2$$

$$H + O_2 + M \longrightarrow HO_2 + M$$

$$HO_2 + NO \longrightarrow OH + NO_2$$

$$NO_2 + h\nu \longrightarrow NO + O$$

$$O + O_2 + M \longrightarrow O_3 + M$$

$$\text{Net}: CO + 2O_2 \longrightarrow CO_2 + O_3 .$$

During Antarctic spring, NO cannot achieve its sufficient concentration due to the following reasons ;

NO, NO_2 and N_2O are formed by the following reactions :

(i) $N_2 + O_2 \quad 2NO.$

It is an endothermic reaction. Equilibrium concentration of NO is only favoured at higher temperature.

(ii) NO_2 arises from NO and Nitrate or Nitrite salts by heating as follows :

$$2NO + O_2 = 2NO_2 ,$$

$$4HNO_3 = 4NO_2 + 2H_2O + O_2 ;$$

(iii) N_2O arises from NH_4NO_3 by heating :

$$NH_4NO_3 = N_2O + 2H_2O .$$

All the above reactions occur relatively at higher temperature. During Antarctic spring, the low temperature disfavours the formation of oxides of nitrogen. Again atmospheric conditions favour the absorption of oxides of nitrogen from the atmosphere as given by Mitra [22].

(i) $ClO + NO \longrightarrow ClNO_2$

(ii) $ClO + NO_2 \longrightarrow ClNO_3$

(iii) $NO_2 + OH + M \longrightarrow HNO_3 + M$

(iv) At low temperature (−9°C) NO_2 forms N_2O_4 crystals.

$$2NO_2 \overset{-9°C}{=} N_2O_4 .$$

Thus, the low concentration of NO instead of production of ozone directly deplets ozone as follows [23]:

$$O_3 + NO \longrightarrow NO_2 + O_2 .$$

Tropospheric low concentrations of NO also affect the oxides of nitrogen by a little amount. Absorption reaction of oxides of nitrogen also occurs in the stratosphere. Tropospheric ozone depletion also affects the total ozone value. So the above tropospheric reactions are also important. The following special atmospheric conditions during Antarctic spring are responsible for the above reactions causing dramatic decrease in ozone concentration. (i) During this period, temperature becomes very low [24]. (ii) Cl_x and ClO_x concentrations are elevated. (iii) NO_x concentrations become low. (iv) Occurrence of large amounts of PCSs. It is supported by the National Science Foundation National Ozone Experiment (NOZE) expedition in the austral spring of 1986 and the collected ground based spectroscopic data in the near UV, visible, middle-IR and millimeter wave regions and balloon-borne, *in situ* O_3 and temperature data [24]. The result is as follows : (i) OClO and ClO densities were elevated [25, 26]. (ii) NO_2 column concentrations were low [27]. (iii) Chlorine-chemistry was perturbed [28].

Scattered diagram of ozone concentration with Solar Flare Number is represented in Figure 3. We see that the nature of ozone variation with Solar Flare Numbers is oscillatory. From correlation coefficient (Table 1), we see that correlation coefficients between monthly mean ozone concentration and monthly mean Solar Flare Number is poor. This shows that Antarctic ozone depletion is independent of Solar Flare Number. But generally, ozone depletion should increase with increase of solar activity. Negative correlation is expected. In case of January and February, we get the negative correlation, but poor. Some special chemical processes play an important role to control the formation and destruction processes of ozone. Hence, the effect of solar parameters and the chemical processes on O_3 concentration are comparable. So oscillatory nature is quite expected.

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